

Selective catalytic reduction of NO with NH₃ at low temperatures over iron and manganese oxides supported on mesoporous silica

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Abstract

A series of catalysts of iron–manganese oxide supported on mesoporous silica (MPS) with different Mn/Fe ratio were studied for low-temperature selective catalytic reduction (SCR) of NO with ammonia in the presence of excess oxygen. Effects of amounts of iron–manganese oxide and calcination temperatures on NO conversion were also investigated. It was found that the Mn–Fe/MPS with Mn/Fe = 1 at the calcination temperature of 673 K showed the highest activity. The results showed that this catalyst yielded 99.1% NO conversion at 433 K at a space velocity of 20,000 h^{−1}. H₂O has no adverse impact on the activity when the SCR reaction temperature is above 413 K. In addition, the SCR activity was suppressed gradually in the presence of SO₂ and H₂O, while such effect was reversible after heating treatment.

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1. Introduction

The major technology for reducing nitrogen oxide emissions from stationary sources is selective catalytic reduction (SCR) of NO_x ($x = 1$ and 2) by ammonia. The general reaction is as follows: $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$. In power plant, however, a drawback inherent to the use of SCR is the SO₂ and dust present in the flue gas. Considering the problem of SO_x-deactivation, a new efficient catalyst for low-temperature SCR is greatly needed. This catalyst could be placed downstream of the dust catcher and desulfurizer without preheating the flue gas. Moreover, there is still residual SO₂ remaining after desulfurizer, so residual SO₂ should be considering. In recent researches, Mn-based catalysts show good activity for low-temperature NO reduction with NH₃. Examples of these catalysts are MnO_x/Al₂O₃ [1,2], MnO_x/TiO₂ [3–5], MnO_x/NaY [6], MnO_x/AC [7–9], and MnO_x/USY [10]. The SCR activity of different pure manganese oxides also was investigated [11,12]. Mixed oxides containing Fe and Mn as main metal element have been reported to be active for SCR reaction [3]. On the other hand, mesoporous silica holds high specific surface area

ranging 500–1400 m² g^{−1} and nanopores of several nm in diameter even after the hydrothermal treatment [13]. Mesoporous silica is known to be more resistant to sulfur poisoning. The stability of sulfates on the mesoporous silica surface is weaker than that on other metal oxides. Therefore, we have investigated iron–manganese oxide supported on mesoporous silica catalysts as low-temperature SCR catalysts.

2. Experimental

2.1. Preparation of catalysts

The catalyst support of mesoporous silica (MPS) was prepared as follows. To a mixture of distilled water (80 g), ethanol (64 g), and cetyltrimethylammonium bromide (40 g) which had been adjusted to pH = 10 with tetramethylammonium hydroxide (25 wt.% aqueous solution) and then aged at 333 K in water bath for 1 h, tetraethoxysilane (25 g) was added. The mixture was stirred for 48 h at 293 K. The resulting precipitate was separated by filtration under suction, washed with distilled water, evaporated to dryness at 393 K, followed by calcination in air at 873 K for 4 h to remove the template. As catalyst sources, ferric nitrate and manganese acetate were used. The catalysts were impregnated with an aqueous solution of ferric nitrate and manganese acetate. The impregnated

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catalysts were first dried at 393 K for 3–4 h, followed by calcinations at 673–973 K in air for 6 h. The percent of metals Fe and Mn is based on the support.

2.2. Characterization of the catalysts

Specific surface area, pore volume and pore size distribution of the catalysts were measured using nitrogen adsorption at 77 K and determined by BET and BJH methods using a NOVA 4000 automated gas sorption system. Prior to the surface area and pore size distribution measurements, the samples were degassed in vacuo at 623 K for 24 h. The powder X-ray diffraction (XRD) measurement was carried out on a Rigaku D/max-III A system with Cu K α radiation.

2.3. Catalytic activity measurement

The SCR activity measurement was carried out using a quartz tubular downflow reactor (25 mm in i.d. and 400 mm in length) inserted with a thermometer. The reaction conditions were as follows: 1000 ppm NO, 1200 ppm NH₃, 3% O₂, 10% water vapor (when used), 250 ppm SO₂ (when used), balance N₂, 1200 ml/min total flow rate, and gas hourly space velocities (GHSV) = 20,000 h⁻¹ (ambient conditions). The premixed gases (10% NO/N₂, 10% NH₃/N₂, and 10% SO₂/N₂) were prepared used to formulate the flue gas in laboratory. Water vapor was generated by passing N₂ through a gas-wash bottle-containing deionized water. Before entering the reactor, the feed gases were mixed in a glass chamber, but NH₃ in N₂ was fed directly into the reactor by passing the mixing chamber to avoid possible reaction between SO₂ and NH₃ before the catalyst bed. The NO and NO₂ concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap-containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. All the data were obtained after 60–200 min when the SCR reaction reached steady state. The catalytic activities for NO oxidation to NO₂ were also measured. The reaction conditions were as follows: 1000 ppm NO, 3% O₂, balance N₂, 1200 ml/min total flow rate, and gas hourly space velocities (GHSV) = 20,000 h⁻¹ (ambient conditions). Another difference from the SCR activity measurement was that the O₂ was fed directly into the reactor by passing the mixing chamber to avoid possible reaction between O₂ and NO before the catalyst bed. NO conversion to NO₂ was obtained by this equation: NO conversion to NO₂ = (([NO_x] – [NO])/[NO_x]) \times 100%, where NO_x represents NO + NO₂.

2.4. FT-IR and TGA analyses

Fourier transform infrared spectroscopy (FT-IR) was used to determine sulfur-containing species formed on catalyst surface. A Bruker EQUININOX55 spectrometer was used at ambient temperature. The fresh, used 30% Mn–Fe/MPS catalyst after

the SCR reaction in the presence of H₂O and used 30% Mn–Fe/MPS catalyst under H₂O and SO₂ were analyzed. Before the analyses, the sample was ground, mixed, and palletized with potassium bromide with a sample to potassium bromide ratio of 1:100. For the used catalysts after the SCR reaction, the sample was purged in N₂ at the reaction temperature for 4 h to remove physically adsorbed species and then cooled to room temperature. The heating treatment of the used sample was carried out in N₂ at 773 K for 4 h, which was also analyzed by FT-IR.

To provide further evidence for the identification of the deactivating agents formed on the catalyst surface during the course of the reaction under H₂O and SO₂, thermogravimetric analysis (TGA) was carried out using a Thermobalance METTLER Toledo Model SDTA 851. Measurements were performed over 4 mg of sample under an inert atmosphere of N₂, in the temperature range RT ~1070 K at a rate of 10 K min⁻¹.

3. Results and discussion

3.1. Catalyst characterization

The specific surface area, pore volumes, and pore sizes of Mn–Fe/MPS catalysts with Mn/Fe = 1 are summarized in Table 1. From Table 1, we can see that the specific surface area of the support of MPS is the largest of all the samples. Once the iron–manganese oxide was loaded on it, the specific surface area has an obvious decrease. Furthermore, the specific surface area of Mn–Fe/MPS was greatly affected by the calcination temperature, and decreased with the calcination temperature rising. The Mn–Fe/MPS at the calcination temperature of 973 K has the smallest specific surface area (100 m² g⁻¹) and the pore diameter of it increases to 9.65 nm while others are between 2.65 and 3.65 nm.

The calcination temperature has great effect on the crystallinity as well as specific surface area of the catalysts. The XRD patterns of the Mn–Fe/MPS with Mn/Fe = 1 in Fig. 1 shows the influence of calcination temperature. The total loading of Mn–Fe on the MPS is 30%. At low loadings (<15%), no visible manganese oxide phase can be observed. This may be due to the poor crystallinity of the catalysts, and the amorphous phase may have formed in the catalyst particles. However, as calcination temperature was increased, the crystal phase of Fe₂O₃ became apparent, and we can observe apparent crystal phase of Fe₂O₃ from the XRD pattern of Mn–Fe/MPS calcined

Table 1
Characterization of the Mn–Fe/MPS catalysts calcined at different temperatures

Samples ^a	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
MPS (873 K)	980	1.11	2.65
Mn–Fe/MPS (673 K)	460	0.47	2.86
Mn–Fe/MPS (773 K)	400	0.40	3.05
Mn–Fe/MPS (873 K)	280	0.29	3.65
Mn–Fe/MPS (973 K)	100	0.11	9.65

^a The number in the parenthesis is the calcination temperature.

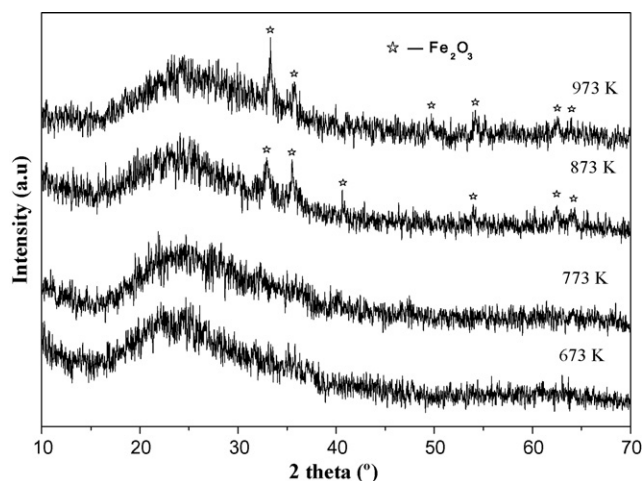


Fig. 1. XRD patterns of Mn-Fe/MPS catalysts calcined at different temperatures.

at 873 K. But the manganese oxide phase has not yet formed even at the calcination temperature of 973 K. From Fig. 1 we can conclude that the manganese oxides have good dispersion on the MPS despite the calcination temperature.

3.2. Effect of Fe/Mn ratio on SCR activity

Five samples of Mn-Fe/MPS were used to study the effect of Fe/Mn ratio on the low-temperature SCR of NO by ammonia. Each sample had the same total Mn-Fe loading of 30% but with a different Fe/Mn ratio. There was only 56–83% conversion when Mn/MPS was used as a catalyst for SCR of NO at 373–455 K. Therefore, Mn and Fe species must play an integrated role in this catalytic reaction. Fig. 2 shows the results of various Mn-Fe/MPS for SCR of NO by ammonia as a function of temperature. It can be observed that the addition of Fe on MPS caused enhancement of the catalytic activity. Increasing Fe proportion increased NO conversion until the Mn/Fe ratio reaches to 1:1. After this level, a further increase Fe proportion did not increase the activity.

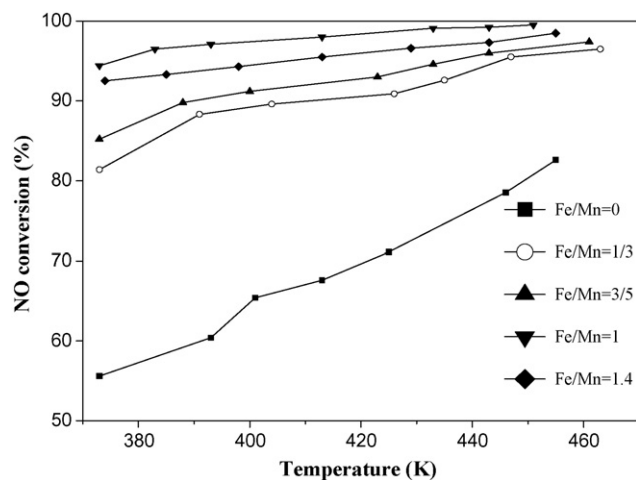


Fig. 2. NO conversion on various Mn-Fe/MPS catalysts with different Fe/Mn ratio. Reaction conditions: [NO] = 1000 ppm, [NH₃] = 1200 ppm, [O₂] = 3%, balance N₂, and GHSV = 20,000 h⁻¹.

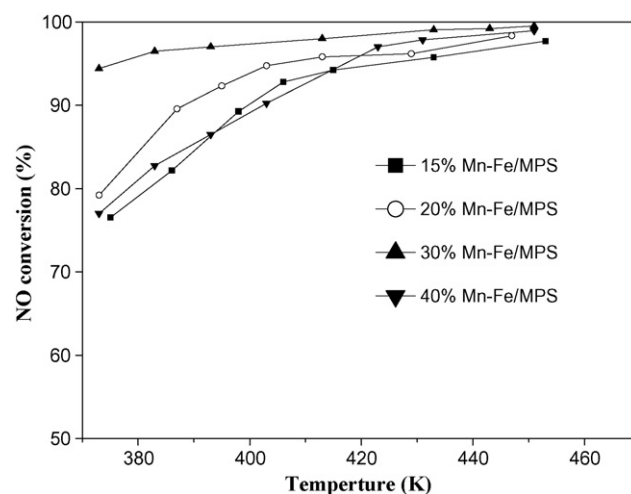


Fig. 3. NO conversion on various Mn-Fe/MPS catalysts with different loading. Reaction conditions: [NO] = 1000 ppm, [NH₃] = 1200 ppm, [O₂] = 3%, balance N₂, and GHSV = 20,000 h⁻¹.

3.3. Effect of total loading of Mn-Fe on SCR activity

To obtain the optimum total loading of Mn-Fe, four samples of Mn-Fe/MPS were used to study the effect of total loading on the low-temperature SCR of NO by ammonia. Each sample had a different total loading with Fe/Mn = 1. Steady state NO conversion data at various temperatures obtained with catalysts of various loading are shown in Fig. 3. The results showed that increasing the total loading had significantly enhanced the NO conversion when the total loading is less than 30%. However, when the total loading of Mn-Fe reaches 30%, increasing the loading of Mn-Fe cannot improve the conversion. It may be that the catalyst performance is related to the specific layers of high-dispersed iron-manganese oxide supported on MPS. When the loading exceed 30%, the interaction between the MPS and iron-manganese oxide becomes feeble and the number of participating surface iron-manganese oxide sites decreases with the loading increasing. From Fig. 3, the optimum total loading of Mn-Fe on Mn-Fe/MPS is 30%.

3.4. Effect of calcination temperature on SCR activity

Based on the preceding catalyst characterization, the calcination temperature has great effect on the characteristics of the catalysts. In this work, we also studied the effect of calcination temperature on SCR activity. As shown in Fig. 4, the catalyst Mn-Fe/MPS (973 K) which was calcined at 973 K showed a very low activity for the low-temperature SCR of NO by ammonia. Even the SCR reaction temperature reaches 473 K, the NO conversion is only 45.6%. From Fig. 4, the catalyst Mn-Fe/MPS (673 K) which was calcined at 673 K showed the highest activity. However, the catalyst Mn-Fe/MPS (773 K) and Mn-Fe/MPS (873 K) which were calcined at 773 K and 873 K showed almost the same activity when the SCR reaction temperatures exceed 433 K. As shown in Fig. 1 and Table 1, the iron-manganese oxide on the Mn-Fe/MPS (673 K) has better dispersion than others and the Mn-Fe/MPS

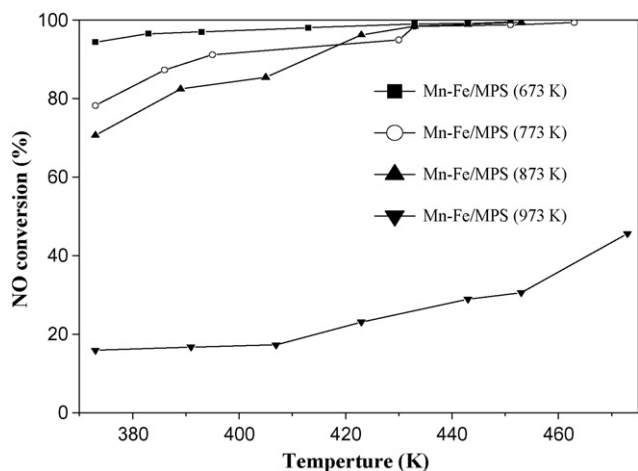


Fig. 4. NO conversion on various Mn-Fe/MPS catalysts calcined at different temperatures. Reaction conditions: $[\text{NO}] = 1000 \text{ ppm}$, $[\text{NH}_3] = 1200 \text{ ppm}$, $[\text{O}_2] = 3\%$, balance N_2 , and GHSV = $20,000 \text{ h}^{-1}$.

(673 K) has the largest specific surface area. All of these contribute to high activity. From Figs. 2–4, 30% Mn-Fe/MPS calcined at 673 K with Fe/Mn = 1 was screened as the optimum catalyst, which would be used in the latter studies.

3.5. Effect of H_2O on SCR activity

Many reported low-temperature catalysts for SCR of NO with NH_3 have the problem of deactivation when water vapor was introduced into fed gas [9,12]. So we studied the effect of H_2O on the SCR activities over Mn-Fe/MPS catalyst. As shown in Fig. 5, when the SCR reaction temperature was 373 K, the NO conversion decreased sharply from 94.4 to 85.6% with the introduction of H_2O . However, such deactivation was suppressed with the SCR reaction temperature increasing. When the SCR reaction temperature reached 413 K, the NO conversion decreased only 0.2%. From Fig. 5, H_2O has no adverse impact on the activity when the SCR reaction temperature is above 413 K. To verify this result, all the data

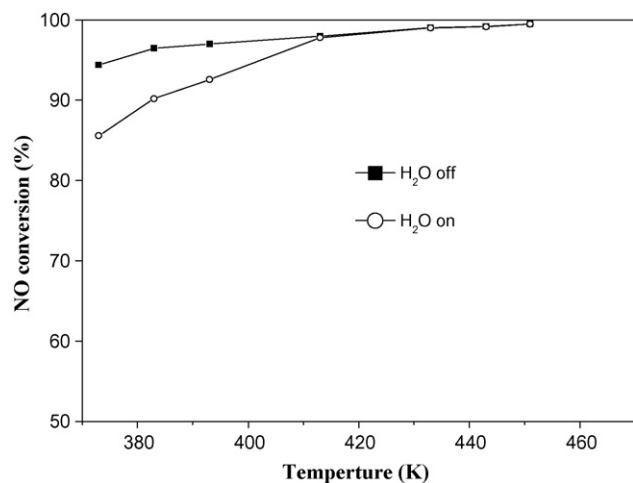


Fig. 5. Effect of H_2O on No conversion over 30% Mn-Fe/MPS. Reaction conditions: $[\text{NO}] = 1000 \text{ ppm}$, $[\text{NH}_3] = 1200 \text{ ppm}$, $[\text{O}_2] = 3\%$, $[\text{H}_2\text{O}] = 10\%$ (when used), balance N_2 , and GHSV = $20,000 \text{ h}^{-1}$.

of the activity tests under 10% H_2O were obtained after 12 h when the SCR reaction reached steady state.

The above results indicate that the Mn-Fe/MPS catalysts are highly active for the low-temperature SCR reaction and H_2O has no adverse impact on the activity when the SCR reaction temperature is above 413 K. According to Morales et al. [14], the manganese ferrite (MnFe_2O_4) which would be formed in air at temperatures over around 1173 K could not be formed in the Mn-Fe/MPS (673 K) catalyst in our work. So we can detach the high activity from the formation of the manganese ferrite (MnFe_2O_4). From the XRD and BET results, it appears that the finely dispersed iron-manganese oxide, high specific area and the special pore configuration are the main contributor to the activity. The support of MPS is able to adsorb the reaction substrates and the low-temperature activity of the catalyst results from homogeneous dispersion of active nanoparticles on high specific surface areas of MPS. On the other hand, the superior SCR activity on the Fe-Mn catalyst is probably related to its high activity for NO oxidation to NO_2 at low temperatures [15]. Since the $\text{NO}_2 + \text{NO}$ mixture is very active in reacting with NH_3 adsorbed species at low temperatures [16,17], the formed NO_x can be reduced to nitrogen by NH_3 . In our studies, the NO oxidation over Mn-Fe/MPS was observed (as shown in Fig. 6) and the NO conversion to NO_2 over Mn-Fe/MPS could reach high conversion of 42.8% at the temperature of 433 K, while that over Mn/MPS was only 20.6%. The addition of iron oxide accelerates the oxidation rate of NO to NO_2 , which is known to be more active than NO towards SCR reaction [17]. According to Madia et al. [18], ammonium nitrate can be formed below 453 K. However, it is reported that the selectivity for N_2 could reach to 100% over iron-manganese oxide (Fe/Mn = 1) [3]. Therefore, if there is ammonium nitrate formed during the action, the catalyst would loss activity gradually because of more and more pore structures being plugged and specific surface area reduction. Nevertheless, all along the SCR reaction course in absence of H_2O and SO_2 , the Mn-Fe/MPS catalyst always kept high activity and no deactivation was observed. Even when the H_2O was added above 413 K, the

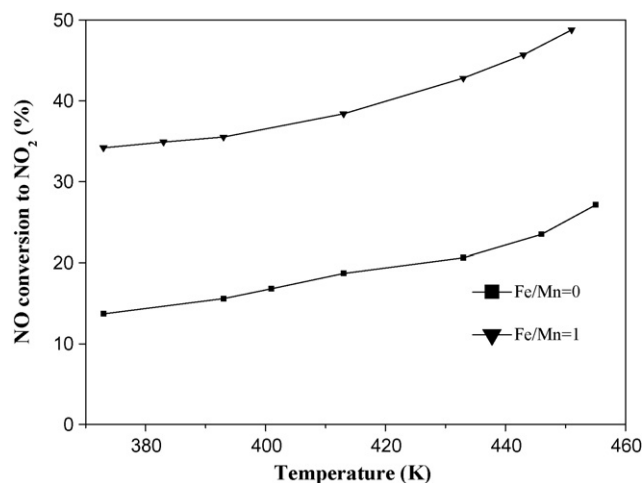


Fig. 6. Oxidation activity of NO to NO_2 by O_2 over 30% Mn-Fe/MPS and 30% Mn/MPS. Reaction conditions: $[\text{NO}] = 1000 \text{ ppm}$, $[\text{O}_2] = 3\%$, balance N_2 , and GHSV = $20,000 \text{ h}^{-1}$.

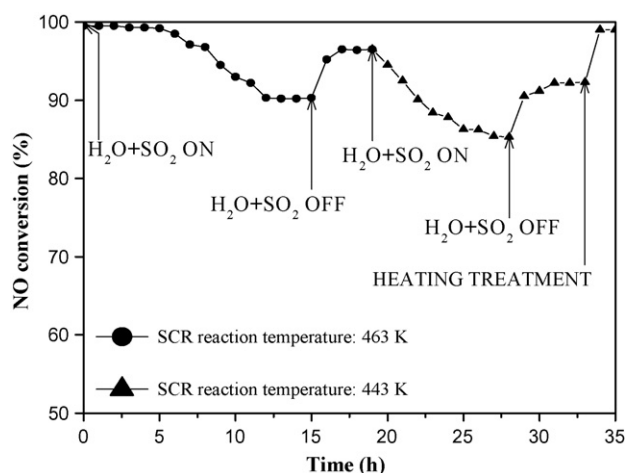


Fig. 7. Synergetic effect of H_2O and SO_2 on NO conversion over 30% Mn-Fe/MPS. Reaction conditions: $[\text{NO}] = 1000$ ppm, $[\text{NH}_3] = 1200$ ppm, $[\text{O}_2] = 3\%$, $[\text{H}_2\text{O}] = 10\%$, $[\text{SO}_2] = 250$ ppm, balance N_2 , and GHSV = $20,000 \text{ h}^{-1}$.

catalyst still kept high activity. In the latter figure of FT-IR spectrum, there is no NH_4^+ detected over the used catalyst while no SO_2 added into the reagent. So it had little chance for ammonium nitrate forming accompanied with the SCR reaction in this work.

3.6. Synergetic effect of H_2O and SO_2 on SCR activity

Because there is still residual SO_2 remaining after desulfurizer, so residual SO_2 should be considering in SCR reaction. The synergetic effects of H_2O and SO_2 on SCR activity in our work are noticeable. As shown in Fig. 7, when 10% H_2O and 250 ppm SO_2 were added to the reactants (the SCR temperature was first kept at 463 K), the NO conversion over Mn-Fe/MPS did not decreased obviously. After 5 h, the NO conversion still kept 99.2% compared to the initial 99.8%. The reason should be that the large surface area was still enough to allow the reaction occurring in a high NO conversion under the conditions used and the deactivation could not be immediately reflected in a decrease of conversion during the first 5 h. But just at then the NO conversion began to decrease apparently which indicates that the deactivation of the catalyst is a progressive and accumulative course. And 11 h later, the NO conversion almost kept a steady level of 90.3%. After 14 h SCR reaction in the presence of H_2O and SO_2 , the H_2O and SO_2 were removed from the fed gases and within 2 h the NO activity restored to 96.5%, which is lower than the initial 99.8%. After another 2 h of steady reaction at 463 K (the NO conversion stabilized at 96.4%), the SCR temperature lowered to 443 K and the H_2O and SO_2 were once again introduced to the fed gases. However, this time the NO conversion immediately decreased. After 8 h SCR reaction when H_2O and SO_2 were fed once again, the NO conversion gradually decreased to 85.4%. Then it took 1 h for the NO conversion decreased from 85.4 to 85.3% and the deactivation was still going on. When the NO conversion lowered to 85.3%, the H_2O and SO_2 were removed from the fed gases and within 5 h the NO activity restored to 92.3%, which is still lower than the initial 96.4%. When the catalyst was heating

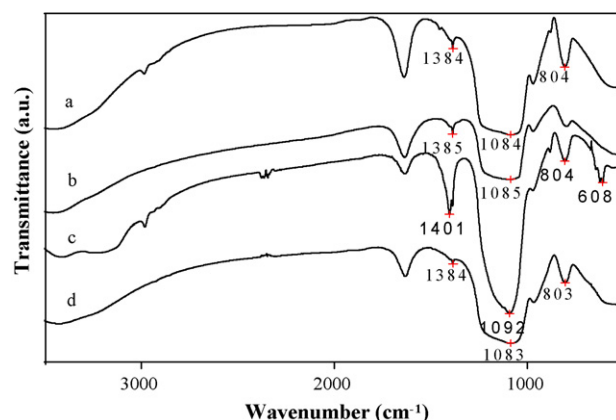


Fig. 8. FT-IR spectra of the fresh (a), used under H_2O (b), used under $\text{H}_2\text{O} + \text{SO}_2$ (c) and heating treated (d) 30% Mn-Fe/MPS.

treated 4 h in N_2 at 773 K, the activity could be restored to 99.1%, almost near the 99.2% conversion at 443 K in the absence of H_2O and SO_2 .

The results clearly indicate that the deactivation of the Mn-Fe/MPS catalyst in the presence of H_2O and SO_2 is due to the catalyst pore plugging and surface area loss because of the NO conversion restoring after heating treatment. In the presence of H_2O and SO_2 , SO_2 can be oxidized to SO_3 by O_2 and NO_2 . The reaction is known as lead chamber reaction. The SO_x compounds ($\text{SO}_2 + \text{SO}_3$) are adsorbed on the transition metal oxides and they are difficult to desorb at low temperatures and sulfate species would be easily formed. The occupation of the active sites by sulfate species would consequently decrease the SCR activity [2]. From Fig. 7, increasing the SCR reaction temperature could slower deactivation of the catalyst.

FT-IR spectra of the fresh, used and heating treated Mn-Fe/MPS catalysts are shown in Fig. 8a–d. The spectrum of the fresh Mn-Fe/MPS catalyst exhibits two IR bands at 1087 and 804 cm^{-1} , which can be assigned to Si–O–Si band. The Mn-Fe/MPS under H_2O showed almost the same spectrum of the fresh one. After the SCR reaction in the presence of H_2O and SO_2 , the Mn-Fe/MPS showed a spectrum roughly similar to that of the fresh one. But a new band appears at 1401 cm^{-1} , which can be assigned to NH_4^+ species chemisorbed on the Brønsted acid sites [19,20]. Simultaneously, a new weak band appears at 608 cm^{-1} , which may be assigned to the characteristic frequencies of SO_4^{2-} ion. Free SO_4^{2-} ion shows two infrared-active bands at 1104 and 613 cm^{-1} [21]. These FT-IR results are consistent with Zhu et al. [22]. Furthermore, the band at 1087 cm^{-1} has shifted to 1094 cm^{-1} , which may be due to that the very narrow Band of SO_4^{2-} ion at 1104 cm^{-1} overlaps with that of Si–O–Si. However, the spectrum of the heating treated sample is almost the same as the fresh catalyst, which showed that the sulfate species formed on the surface of catalyst have been decomposed completely after heating treatment and the SCR activity over the catalyst restored as shown in Fig. 7. From the results above, we can conclude that ammonium sulfate may have been formed during SCR reaction

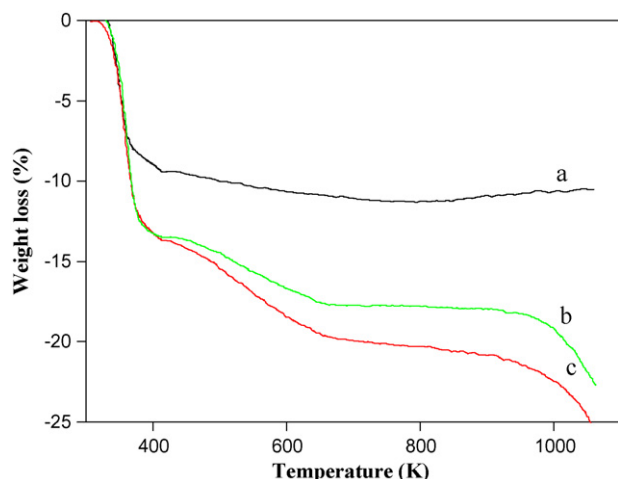


Fig. 9. TGA spectra of fresh catalyst (a), deactivated catalyst (b) and fresh catalyst-containing ammonium sulfate (c).

in the presence of the H_2O and SO_2 . Of course NH_4HSO_4 and/or $(\text{NH}_4)_2\text{S}_2\text{O}_7$ may be formed [23].

Thermogravimetric analysis (TGA) of the deactivated catalyst offered further evidence for the identification of ammonium sulfate formed on the catalyst surface accompanied with the SCR reaction. TGA spectra for the fresh, the deactivated and ammonium sulfate impregnated catalysts are shown in Fig. 9. The deactivated and the possible deactivating—agents-impregnated catalysts have almost the same temperature region of weight loss. The initial loss in the temperature region from 330 to 430 K is due to water desorption on the catalyst surface. The change in catalyst weight in the high-temperature region from 470 to 670 K could be attributed mainly to the ammonia desorption from the decomposition of the ammonium sulfate on the catalyst surface. The weight loss after 920 K may be due to the decomposition of metallic sulfates formed during the heating course of the thermogravimetric analysis accompanied with the decomposition of the ammonium sulfate, while no weight loss of the fresh catalyst was observed after about 440 K.

As the SCR reaction proceeded in the presence of H_2O and SO_2 , more and more sulfate salts would be formed and thus more and more pore structures would be plugged. Although the NO conversion did not decrease obviously as shown in Fig. 7, the deactivation of Mn–Fe/MPS was an accumulative course, and the Mn–Fe/MPS catalyst should be heating treated to recover the activity.

4. Conclusion

The mesoporous silica supported iron–manganese oxide catalysts (Mn–Fe/MPS) were highly active for the low-temperature SCR of NO with NH_3 in the presence of excess oxygen. The Mn–Fe/MPS with Mn/Fe = 1 at the calcination temperature of 673 K showed the highest activity and this catalyst yielded 99.1% NO conversion at 433 K at a space velocity of $20,000 \text{ h}^{-1}$. H_2O has no adverse impact on the activity when the SCR reaction temperature is above 413 K. As the SCR reaction proceeded in the presence of H_2O and SO_2 , excess amount of sulfate salts were formed resulting in the catalyst deactivation gradually and the activity could almost recover to the initial level after heating treatment. The catalyst is substantially superior to any other reported catalyst in terms of integrated performance.

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